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To scale or not to scale : self-capacitance, "Hubbard U" and quantum dot size ?

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Abstract . A seminal question to ask regarding quantum dots is how (if at all) its self-capacitance scales with size. What kind of a phenomenology should guide physicists who are involved in studying Coulomb blockade effects and in the practical task of evolving single electron transistors? Answering these issues involves calculating many body effects in quantum dots. We study the electron-electron interaction within a simplified spherical quantum dot using the local density approximation (LDA) and local spin density approximation (LSDA). We experiment with a variety of confining potentials (triangular, harmonic, square well *etc*) and with a varying number of electrons (N = 2 to 20). We carry out a detailed study of the scaling behaviour of the "Hubbard U", which is a measure of the capacitive energy, with quantum dot size R ($U \sim 1/R^{\beta}$). We find that the scaling exponent β is approximately 1/2 for harmonic confinement and equal to 1 for the square well confinement. We show that the "Hubbard U" depends critically on the shape of the confining potential chosen and size of the quantum dot. It exhibits a weak dependence on the number of electrons. We also examine the relative importance of Coulomb, exchange and correlation terms in the "Hubbard U" and find that correlation plays a relatively more important role at larger size.

Keywords : Quantum dots, self-capacitance, Hubbard U.

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1. Introduction

Quantum dots are structures in which charge carriers are essentially trapped in a 3-dimensional (3D) potential. They are also known as "artificial atoms" [1,2] and consist of a thousand to a million atoms, with system sizes in the range of 1 nm to 10 nm. They are of fundamental and technical interest for next generation electronic devices. An important goal of today's technological drive towards smaller and smaller devices is to fabricate the so called single electron transistor (SET) which can be operational at room temperature [3]. They may also form the basis of new generations of lasers. The emission in quantum dot lasers originates from the recombination of excitonic complexes, so it is important to study and understand the quantum dot's internal electronic structure [4].

Theoretical studies of a QD involve multi-electron effects. These effects have been treated mainly within the local density approximation [5,6] (LDA) of the density functional theory (DFT). Spin-dependent effects have also been taken into account *via* the local spin density approximation [7,8] (LSDA). Since the number of electrons involved in these calculations is small, ranging from 1 to 50, self interaction error [5,7,8] in the LDA may have significant effect on the results. Thus, these systems have also been studied by self-interaction corrected LDA [8]. A large number of these calculations model the system as a 2D circular dot with a harmonic confining potential. There also exist a few calculations which employ the Hartree-Fock (HF) approximation [9], the Thomas-Fermi (TF) approximation [10] and Monte Carlo [11]. We have studied [12] the self-capacitance of a 3D spherical quantum dots in our previous work. We have employed the local density approximation (LDA) and the self-interaction free Harbola-Sahni (HS) scheme [13] in our calculations to study the dependence of shape of the confining potential on the shell structure and the capacitive energy. We have compared capacitive energy calculated using the LDA and the HS scheme. We found that for small number of electrons, the difference is as large as 25. This is due to the self interaction error of the LDA for small number of electrons. Also, we showed that one can calculate the capacitive energy using a more economic route through Janak's theorem. Further, we demonstrated the size dependence of the ground state energy of a single electron system. A preliminary investigation of the "Hubbard U" was also made.

In this work, we investigate the behaviour of the direct Coulomb and the exchange-correlation with the shape of the

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confinement potential and size of the quantum dot. Before we discuss the motivation behind this work, we define a few relevant terms. The "Hubbard U" is composed of a number of terms

$$U = U_c + U_{xc} \tag{1.1}$$

and

$$U_{xc} = U_x + U_{corr} \tag{1.2}$$

where U_c is the direct Coulomb term, U_x is the exchange and U_{corr} is the correlation term. Now,

$$U(N) = N(N-1)U/2 \tag{1.3}$$

$$U = 2U(N)/N(N-1) \tag{1.4}$$

where N is the number of electrons and $U(N)$ could be $U_c(N)$, $U_x(N)$ or $U_{corr}(N)$. $U(N)$ is the effective potential energy of N electron system. In the local density approximation (LDA), all three terms given in eqs. (1.1) and (1.2) are present whereas in certain other approximations, namely, Hartree-Fock (HF) and Harbola-Sahni (HS), the correlation term is absent.

We experiment with various shapes of the confinement potential. Previous quantum mechanical calculations of the capacitance of quantum dots involved disc or cylindrical geometries with parabolic confinement potential [5,6]. The model external potential we have chosen is

$$V_{ext} = \begin{cases} V_0 r^k / R^k - V_0, & r \le R \\ 0 & r > R \end{cases} \tag{1.5}$$

Here, V_0 is the height of the potential. This can be given by the conduction band offset (valence band offset) between the QD and the surrounding layer for the electron (hole). R is the radius of the QD ($2R$ is the width of the potential) and k assumes positive integral values from 1 to say a very large number. Changing the value of k results in the change of the shape of the potential. In particular k = 1 is quasitriangular, k = 2 is quasiharmonic confinement and $k \ge 10$ is quasisquare well confinement. As $k \to \infty$, the potential becomes square well. The capacitive energy is defined as

$$e^2/C(N) = E(N+1) - 2E(N) + E(N-1), \tag{1.6}$$

where $E(N)$ is the total ground state energy of N electron QD. The capacitive energy essentially tracks the "Hubbard U" except for the peaks.

The motivations behind the study of the "Hubbard U" and its constituent terms are both of academic as well as of practical interest. It has long been known [14] that the approximately 1 eV band gap of bulk semiconductors accommodates multiple charge states (MCS) of transition metal impurities. This remarkable telescoping effect means that the Coulomb repulsion is heavily attenuated, by as much as 100 fold, over the atomically expected values. Employing a two band Anderson model, Haldane and Anderson attempted to explain this effect in 1976 [15]. Singh and Vengurlekar [16] provided an analytic framework to understand the success of the Haldane-Anderson model. In another independent work, Anderson demonstrated that the "Hubbard U" can assume negative values if electron lattice interaction is invoked [17]. He exploited this model to explain the absence of paramagnetism in certain amorphous systems. In 1985, Katayama-Yoshida and Zunger [18] reported that the interstitial chromium impurity in a silicon lattice may assume negative effective U. They proposed a microscopic mechanism - stabilization of electron-rich configurations through exchange interaction. Their report was based on a self-consistent local-spin-density Green's function calculation. The negative effective U implies that the attractive exchange-correlation will outweigh the repulsive Coulomb part.

There have been earlier studies of exchange-correlation effects in QDs. Lee *et al* [19], have found that in certain cases the Hartree approximation yielded unphysical negative capacitive energy. More interestingly, Henderson *et al* [20] used coupled cluster singles and doubles (CCSD) method in their study and showed that the correlation effects are significant, having a particular effect on the capacitive energy especially for less confined systems. The tremendous interest in quantum capacitance and the single electron transistor has motivated us to investigate whether the Coulomb interaction in confined systems such as quantum dots exhibits anomalous behaviour akin to those mentioned in this and the previous paragraph.

Experimental studies [21,22] too have indicated the importance of exchange-correlation effects. Experimentally the capacitive energy and hence the "Hubbard U" is found to be equal to the difference between the ionization potential and electron affinity *i.e.*

$$e^2/C(N) = I(N) - A(N). \tag{1.7}$$

In chemistry, this difference is known as the chemical hardness. More the chemical hardness the more stable an atom or molecule is. The "Hubbard U" has also been found to be useful in explaining the abundance spectra [23] of alkali metal clusters.

In this paper, we study the electron-electron interaction within a simplified spherical quantum dot using the local spin density approximation (LSDA). We experiment with a variety of confining potentials (triangular, harmonic, square well *etc.*) for the electrons (see eqn. (1.5). We carry out a detailed study of the scaling behaviour of the "Hubbard U", which is a measure of the capacitive energy, with quantum dot size R. Our main thrust is to study the size dependence of the Coulomb and exchange-correlation for two distinct and extensively used shapes of the potential namely harmonic (k=2) and square well ($k \ge 10$). We also compare our LSDA results with LDA and the HS scheme and state the results.

2. Results

In our calculations we have treated exchange-correlation effect in its Gunnarsson-Lundqvist [24] parameterized form. Our calculations have been performed in atomic units. Unless otherwise stated, all the results are based on LSDA calculations. The scaling exponents reported in this section have been extracted using the Levenburg-Marquardt procedure. Figure 1 shows an overview of shell filling effects. In this we depict the capacitive energy $\left(e^2/C(N)\right)$ as a function of the total number of electrons (N) for quantum dot size $R = 8$ and $k = 1, 2$ and 10. In the inset a similar plot is shown for $k = 4$, 8 and 10. Here, $k = 1$ represents quasitriangular confinement, $k = 2$ quasiharmonic confinement and as we approach large value of k, *e.g.* $k = 8$ or 10, the potential can be considered as a quasisquare well confinement (see eq. (1.5)). We fill electrons in the dot according to the Hund's rule and demonstrate the complete electronic structure of our model quantum dot. From the figure we obtain several facts which are described below.

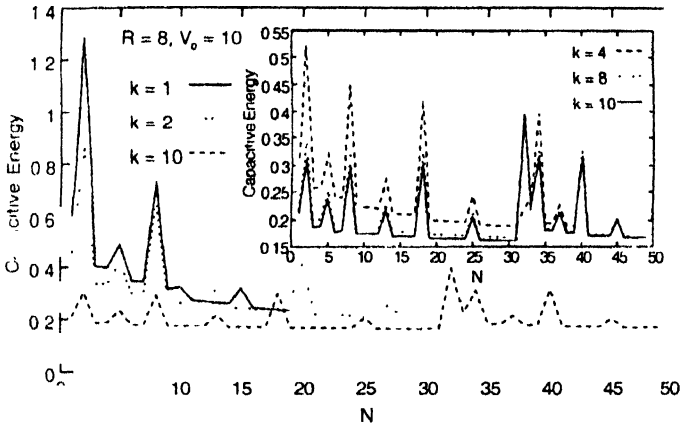

Figure 1. Capacitive energy $e^2/C(N)$ as function of total number of charges N for $k = 1$, 2 and 10, *i.e.* for quasitriangular, quasiharmonic and quasisquare well confinements. The size considered is $R = 8$. Electrons are filled according to the Hund's rule. Smaller peaks correspond to half filled shells whereas larger peaks correspond to filled shells. In the inset, we have shown the capacitive energy as a function of N for $k = 4$, 8 and 10 *i.e.* increasing degree of quasisquare confinement. Notice that the shell structure changes as the shape of the potential changes.

The figure reveals peaks at certain specific values of N. These peaks correspond to either filled or half filled shells. Thus the term "artificial atom" for a quantum dot stands justified. An interesting point is that the smaller peaks in the capacitive energy correspond to half filled shell and larger peaks correspond to completely filled shell structures. For smaller k (*e.g.* $k = 1, 2$), the height of the peaks decreases with N whereas for larger k (*e.g.* $k = 8$ and 10), the heights of the peaks are either equal or at times show a slight increase with N. This implies that the inclusion of many body effects decreases the level spacing. The shell structure changes with the change in the shape of the confining potential. The electronic configurations according to Hund's rule for three distinct confinement potentials and for size $R = 8$ are as follows: For quasitriangular, $1s^{1\uparrow}$, $1s^{1\downarrow}$, $2p^{3\uparrow}$, $2p^{3\downarrow}$, $2s^{1\uparrow}$, $2s^{1\downarrow}$, $3d^{5\uparrow}$, $3d^{5\downarrow}$; for quasiharmonic, $1s^{1\uparrow}$, $1s^{1\downarrow}$, $2p^{3\uparrow}$, $2p^{3\downarrow}$, $3d^{5\uparrow}$, $3d^{5\downarrow}$, $2s^{1\uparrow}$, $2s^{1\downarrow}$, $4f^{7\uparrow}$, $4f^{3\downarrow}$ and for quasisquare, $1s^{1\uparrow}$, $1s^{1\downarrow}$, $2p^{3\uparrow}$, $2p^{3\downarrow}$, $3d^{5\uparrow}$, $3d^{5\downarrow}$, $4f^{7\uparrow}$, $4f^{7\downarrow}$, $2s^{1\uparrow}$, $2s^{1\downarrow}$, $3p^{3\uparrow}$, $3p^{3\downarrow}$, $4d^{5\uparrow}$, $4d^{5\downarrow}$. As we change the shape from $k = 1$ to $k = 2$ and to $k = 10$, the $2s$ shell jumps one shell ahead. With change in the shape of the confinement the maximum number of electrons the dot can accommodate, changes. The total number of electrons N_{max} accommodated by the dot for $k = 1$, 2, 4, 8 and 10 is found to be 20, 30, 40, 48 and 50 respectively. Further, for a given shape of the potential the number of electrons accommodated by the dot decreases as R decreases. For example, for $R = 4$ and $k = 1, 2, 4, 8$ and 10 the total number of electrons accommodated by the dot is $N = 8$, 13, 18, 23 and 25 respectively. The capacitive energy is always lower for a given number of electrons when k is larger. One may understand this as follows. When k is large the confinement is reduced and the effective size of the dot is large. $C(N) \sim R_{\text{eff}}$, and thus the capacitive energy $\sim 1/R_{\text{eff}}$. In particular we find exact agreement of our shell structure for $k = 2$ (quasiharmonic confinement) with the LSDA calculations on spherical quantum dot with harmonic confinement and consequent shell structures of Jiang *et al* [8].

In most of the cases we found that the dot accommodates the right number of electrons so that the last occupied shell or sub-shell is either half filled or completely filled. It is found however that for $R = 8$, $k = 2$, the $4f^{\downarrow}$ level is partially filled. A similar situation is observed for $k = 8$, $4d^{\downarrow}$ level. *This implies that the spherical quantum dot may be electronically unstable and may undergo distortion. This is suggestive of a Jahn-Teller like effect in quantum dots.*

We have performed these calculations using LDA also. The difference between LDA and LSDA is the disappearance of the smaller or secondary peaks that appear in the capacitive energy plot. These secondary peaks are normally attributed to the manifestation of Hund's first rule that favours the maximum spin for half filled shells, making them extra stable.

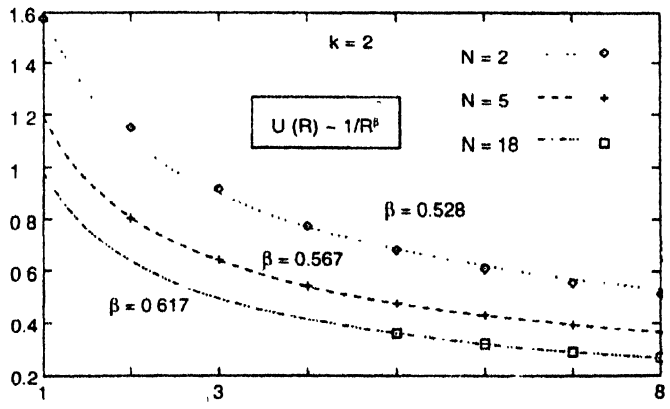

Figure 2. The effective electron-electron interaction energy U, is depicted as a function of size (R) of a QD for three different values of the total number of electrons N and for $k = 2$ (quasiharmonic confinement). The interaction energy $U \sim 1/R^{\beta}$ with the exponent $\beta = 0.528$, 0.567 and 0.617 for $N = 2$, 5 and 18 respectively. Notice the weak dependence of β on N.

Now looking carefully at the capacitive energy plot we infer that capacitive energy (excluding the peaks), which tracks the "Hubbard U" approximately, decreases gradually with increasing N. The rate with which it decreases is different for different size of the dot and the shape of the confining potential. Next we investigate how U and the individual terms comprising it (see eq. (1.1)) scale with R for different shapes of the confinement.

To understand the scaling behaviour, in Figure 2 we plot the "Hubbard U" with size (R) of the QD, for the number of electrons, $N = 2, 5$ and 18 and $k = 2$ (quasiharmonic confinement). "Hubbard U" is the average electron-electron interaction energy in a many electron quantum dot. This figure reveals that U scales as

$$U \sim 1/R^{\beta}, \tag{2.1}$$

where the exponent $\beta = 0.53, 0.57$ and 0.62 for $N = 2, 5$ and 18 respectively.

Figure 3 shows how the individual terms in U scale with size. The external confining potential is quasiharmonic ($k = 2$). The Coulomb term drops with size while the exchange-correlation plays a compensating role. In other words the roles of Coulomb and exchange-correlation are antithetical. For small size, U_{xc} becomes increasingly attractive while the Coulomb term becomes increasingly repulsive. For $N = 2$, $U_c \simeq 2|U_{xc}|$ which is to be expected. As the electron occupancy N increases, the magnitudes of U_{xc} and U_c become smaller. However the compensating nature of the two terms is not affected. A Levenburg-Marquardt least squares fit reveals that

$$U_c \sim 1/R^{\gamma} \tag{2.2}$$

where the exponent $\gamma = 0.49, 0.55$ and 0.61 for $N = 2, 5$ and 18 respectively. U_{xc} follows a similar scaling behaviour *i.e.* $U_{xc} \sim -1/R^{\delta}$ with the exponent values $\delta = 0.45, 0.50$ and 0.55 for $N = 2, 5$ and 18 respectively. Both the exponents γ and δ are approximately 1/2 for quasi-harmonic confinement.

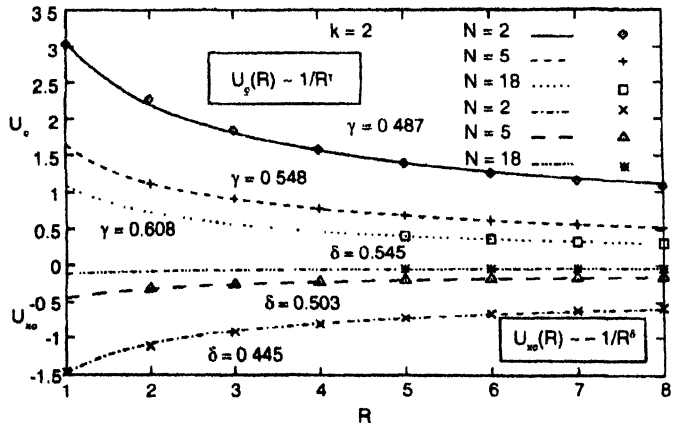

Figure 3. The individual terms in U, Coulomb U_c and exchange-correlation U_{xc} are depicted as a function of size (R) of a QD for three different values of the total number of electrons N and for $k = 2$ (quasiharmonic confinement). The values of N and k are the same as in Figure 2. The Coulomb term scales as $U_c \sim 1/R^{\gamma}$. The exchange-correlation scales as $U_{xc} \sim 1/R^{\delta}$. Note that the exponents increase slightly with N.

Now for completeness of our study, we would like to investigate the scaling behaviour for other shapes of the confinement, for example quasisquare ($k = 10$) and quasitriangular ($k = 1$) *etc.* These results are displayed in Table 1. The effect of the confining potential on the scaling exponent β is dramatic. Whereas for $k = 2$, $\beta \sim 1/2$, as $k \to \infty$, $\beta \to 1$. This latter result may be understood in classical terms ($C \sim R_{eff}$). Interestingly for the quasitriangular confinement ($k = 1$), the scaling exponent is approximately 1/3. We note that with increasing N, β increases. This is due to the fact that with increasing N the effective potential becomes more flat as the effective size of the quantum dot increases. In other words because of the spatial extension of the effective potential, electrons find more space to move and hence Coulomb interaction becomes weaker. With these results we see that the "Hubbard U" actually depends on a number of variables namely the shape of the confinement, the number of electrons and also on size of the quantum dot. We find the following relationship between the exponent β and the confining parameter k:

$$\beta(k) = 0.92\left(1 - 0.78\exp\left[-0.27k\right]\right). \tag{2.3}$$

In Table 1, we also display the exponents γ and δ for the Coulomb and exchange-correlation. This establishes scaling laws for U_c and U_{xc}. Further, we also investigate how the

Table 1. The "Hubbard U" is found to scale as $\sim 1/R^{\beta}$. Similarly the Coulomb and exchange-correlation energy scale as $\sim 1/R^{\gamma}$ and $\sim 1/R^{\delta}$ respectively. The exponents β, γ and δ depend on the shape of the potential, indexed by k (see eqn (1.5)). This table lists the values of β, γ and δ for different values of k and for $N = 2, 5$. Note that the exponents increase from 1/3 to 1 as k increases from 1 to 10.

N		β		
2	1	0.386	0.355	0.325
	2	0.528	0.487	0.445
	4	0.721	0.660	0.601
	8	0.862	0.784	0.710
	10	0.894	0.812	0.735
5	1	0.393	0.381	0.351
	2	0.567	0.548	0.503
	4	0.746	0.718	0.653
	8	0.884	0.846	0.762
	10	0.917	0.877	0.787

"Hubbard U" depends on the number of electrons. We know that classically there should not be any N dependence in U. However, we do find a weak N dependence. Assuming that the exponent β in the scaling of U, has a N dependence so that

$$\beta(N) \sim N^{\eta}, \tag{2.4}$$

then

$$\ln \beta \sim \eta \ln N. \tag{2.5}$$

A logarithmic plot of as a function of N gives the value of η between 0.05 and 0.08 which is very small. This result has phenomenological implication. In experiments on nearly spherical quantum dots one may now safely assume that U – the difference in the electron affinity and the ionization potential, is essentially unchanged with the shell filling.

3. Conclusions

Our detailed calculations suggest that the shell structure is sensitive to the confinement potentials. More interestingly for certain confinement potentials, incomplete filling of degenerate levels is observed. This implies that the spherical quantum dot may be electronically unstable and may undergo distortion. This is suggestive of a Jahn-Teller like effect in quantum dots. We reiterate that as the system size becomes larger (or the electron density spreads out more) a more accurate analysis would require the use of asymptotically correct exchange-correlation potential in place of LSDA. The latter is not accurate in the outer regions of a system. The scaling of U, U_c and U_u strongly depends on the shape of the confining potential. Exchange-correlation does play an important role in the scaling of "Hubbard U" but it does not show any anomalous bahaviour as to outweigh the Coulomb interaction and make the overall U negative. In particular, correlation is more sensitive to the quantum dot size and the shape of the confinement. It has long been understood that electron correlation is of critical importance in atoms, molecules and solids and it should also be so in quantum dots. This stands justified through our calculations.

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